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Kinetic studies on sterically hindered pentaaminecobalt(III) complexes. Synthesis, anation reactions and crystal structure of $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$

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Abstract

The sterically hindered pentakis(ethylamine)aquacobalt(III) complex has been prepared and its perchlorate dihydrate salt characterized by X-ray spectroscopy. Anation reactions of this complex with Cl^-, Br^-, CF_3COO^-, $H_2PO_4^-$ and H_3PO_4 have been studied as a function of temperature, and the results compared with those previously obtained for other $[Co(RNH_2)_5H_2O]^{3+}$ (R = H, Me) systems. Comparison of the bond distances of the title compound with those of the corresponding pentaammine complex leads to the conclusion that the increasing steric demands of the am(m)ine ligands are responsible for the clear rate acceleration observed in the dissociative activation anation process.

Introduction

Substitution reactions on $[Co(NH_3)_5H_2O]^{3+}$ have been thoroughly studied [1]. There is no doubt about the intimate mechanism that operates for these reactions – a dissociatively activated interchange [2]. On the other hand, studies dealing with acid and base hydrolysis of the sterically hindered $[M(MeNH_2)_5Cl]^{2+}$ (M = Co, Cr, Rh) complexes have been attracting much attention in recent years [3]. A correlation between ground state properties and rate constants for base-catalyzed hydrolysis has also been very recently found for macrocyclic pentaaminecobalt complexes [4].

We have already dealt for the first time with the steric effects on a series of anation reactions of $[Co(RNH_2)_5H_2O]^{3+}$ (R = H, Me) complexes [5], and shown that a definite increase of the reaction rates is present. This can be associated to the greater steric demands of the amine versus ammine ligands. Here we report a series of anation reactions on the $[Co(EtNH_2)_5H_2O]^{3+}$ ion, as well as the crystal structure of its perchlorate salt, in order to compare the steric effect of the changes in the amine substituent in the reaction mechanism as well as its relation to the ground-state properties.

Experimental

Reagents

Caution: Special care must te taken on handling perchlorate salts of compounds containing organic ligands, as there is a high risk of explosion. $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$ was prepared by treatment of a solution of 0.6 g of $[Co(EtNH_2)_5Cl](ClO_4)_2$ [6] in 50 cm³ of 0.1 M $HClO_4$ with 5 cm³ of a solution of $AgClO_4$ (10% in excess). After continuous stirring at 40 °C for *c.* 4 h the AgCl formed is filtered and the solution evaporated under vacuum at 35 °C to *c.* 10 cm³. A few drops of concentrated cold $HClO_4$ are added and the solution is kept in the refrigerator for 12 h on which a red solid is formed. On recrystallization in 0.1 M $HClO_4$ good crystals are obtained and dried in a dessicator. Yield 43%. *Anal.* Calc. for $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$: C, 18.8; H, 6.4; N, 11.0. Found: C, 18.7; H, 6.2; N, 10.9%. UV–Vis spectrum in 0.1 M $HClO_4$ $\lambda_1 = 516$ nm ($\epsilon_1 = 87$ M^{-1} cm^{-1}), $\lambda_2 = 364$ nm ($\epsilon_2 = 87$ M^{-1} cm^{-1}). Specimens for X-ray analysis could be easily found, but, when removed from the mother liquor, they inevitably broke on standing. For this reason a few specimens were selected and sealed in Lindemann capillary tubes. Solutions of LiBr, LiCl,

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$LiCF_3COO$, LiH_2PO_4, $LiClO_4$ and $HClO_4$ were prepared and standardized as previously described.

Kinetics

UV–Vis spectra were recorded on an HP8452A instrument equipped with a thermostated (±0.2 °C) multicell transport. Reactions were followed in the full 600–325 nm range. Observed rate constants were derived from the absorbance versus time traces at the most appropriate wavelengths. Good retention of isosbestic points was observed during the time in which the reactions were monitored (2–3 half lives).

All kinetic runs were performed under pseudo-first order conditions ($[Co] = 1\text{–}5 \times 10^{-3}$ M). Solutions for the kinetic runs as well as data treatment of the rate constants were done as previously described [5, 7].

Crystal structure

A non-stable prismatic crystal (0.2×0.2×0.3 mm) was selected, sealed in a Lindemann capillary tube and mounted on a Philips PW-1100 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8 \leqslant \theta \leqslant 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using $\omega/2\theta$ scan technique. A total of 4256 reflections was measured in the range $2 \leqslant \theta \leqslant 25$; 1662 reflections were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control. Significant intensity decay was not observed. Lorentz polarization but no absorption corrections were made. The structure was solved by Patterson synthesis, using the SHELXS computer program [8a], and refined by full-matrix least-square method, with the SHELX76 computer program [8b]. The function minimized was $\Sigma w \| F_o| - |F_c \|^2$, where $w = (\sigma^2(F_o) + 0.026|F_o|^2)^{-1}$. f, f' and f'' were taken from the International Tables of X-ray Crystallography [9]. A total of 35 hydrogen atoms was computed and their position refined with an overall isotropic temperature factor by using a riding model. The final R factor was 0.067 ($R_w = 0.070$) for all observed reflections. The number of refined parameters was 316. Max. shift/e.s.d. = 0.1; max. and min. peaks in final difference synthesis were 0.4 and −0.4 e Å^{-3}, respectively. Tables 1 and 2 summarize the crystallographic data and the atomic positional parameters for significant atoms, respectively.

TABLE 1. Summary of crystallographic data

Formula	$C_{10}H_{43}Cl_3N_5O_{15}Co$, $[Co(C_2H_7N)_5(H_2O)](ClO_4)_3 \cdot 2H_2O$
Name	aquapentakis(ethylamine)cobalt(III) perchlorate dihydrate
Formula weight	636.75
System	orthorhombic
Space group	*Fdd*2
a (Å)	36.836(6)
b (Å)	33.058(5)
c (Å)	9.150(2)
V (Å)	11142(5)
D_x (g cm^{-3})	1.518
Z	16
$F(000)$	3344.0
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	9.98
T (K)	298
R	0.067
R_w	0.070

TABLE 2. Positional atomic parameters for significant atoms in the crystal structure of $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$

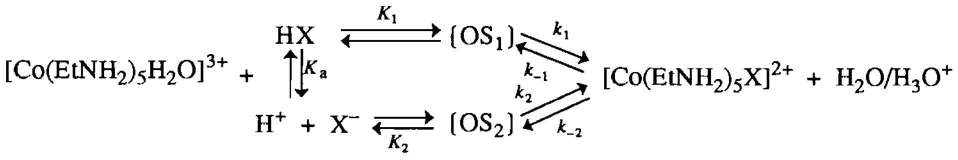
Atom	x	y	z
Co	0.08018(4)	0.03530(4)	0.050000
O	0.1198(2)	0.4016(3)	0.4527(11)
N(1)	0.0664(3)	0.3997(3)	0.6738(14)
N(2)	0.0450(3)	0.3961(3)	0.3801(13)
N(3)	0.0424(3)	0.3270(3)	0.5711(14)
N(4)	0.1169(4)	0.3325(3)	0.6174(13)
N(5)	0.0921(4)	0.3326(3)	0.3265(15)
C(1)	0.0788(6)	0.4437(5)	0.6801(24)
C(11)	0.0589(6)	0.4640(7)	0.8125(22)
C(2)	0.0575(5)	0.4309(5)	0.2873(17)
C(21)	0.0285(5)	0.4547(5)	0.2225(20)
C(3)	0.0087(6)	0.3195(8)	0.5049(29)
C(31)	−0.0143(4)	0.2879(6)	0.5725(25)
C(4)	0.1274(5)	0.3416(5)	0.7664(20)
C(41)	0.1588(5)	0.3166(6)	0.8176(26)
C(5)	0.0934(8)	0.2910(6)	0.3054(28)
C(51)	0.1017(5)	0.2731(5)	0.1652(20)

Results and discussion

For the observed rate constants see 'Supplementary material'. A rate law and reaction scheme, as used for the derivation of first- and second-order rate constants for similar systems, was applied (Scheme 1) [5, 7].

Only for the $H_3PO_4/H_2PO_4^-$ system is the K_1k_1/k_{-1} path detected, and the absence of curvature in all k_{obs} versus $[X]_T$ plots indicate that the product K_2k_2 (or K_1k_1) cannot be separated. Table 3 lists all these values for the systems studied as a function of temperature, acidity and anating species. Thermal activation parameters were derived from standard Eyring plots and the values obtained for the reactions studied are also shown in Table 3.

Comparison of these values with those obtained for the same $[Co(RNH_2)_5H_2O]^{3+}$ (R = H, Me) systems already studied [5] (Table 4) clearly shows an increase in the rate constants on going from R = Me to R = Et.



$\{OS_i\}$ = outer-sphere complex

$$k_{obs} = \frac{K_1k_1[H^+] + K_2k_2K_a}{[H^+] + K_a + (K_1[H^+] + K_2K_a)[X]_T}[X]_T + (k_{-1}[H^+] + k_{-2})$$

$[X]_T$ = total anating species concentration

K_1 or K_2 $\equiv$ K; k_1 or k_2 $\equiv$ k_+; k_{-1} or k_{-2} $\equiv$ k_-

Scheme 1.

TABLE 3. Kinetic parameters obtained for the $[Co(EtNH_2)_5H_2O]^{3+}$ anation reactions studied as a function of temperature and anating species (I = 1.0 M $LiClO_4$, $[H^+]$ = 0.01–0.2 M $HClO_4$)

Anating species	T (°C)	10^4k_+K (M^{-1} s^{-1})	10^4k_- (s^{-1})	$\Delta H^‡_+$ [a] (kJ mol^{-1})	$\Delta S^‡_+$ [a] (J K mol^{-1})	$\Delta H^‡_-$ (kJ mol^{-1})	$\Delta S^‡_-$ (J K mol^{-1})
Br^-	30	22.6 ± 1.2	18.1 ± 0.4				
	40	48.2 ± 3.9	49.2 ± 1.3				
	50	110 ± 9	83.2 ± 3.9	61.1 ± 2.2	−93 ± 7	63.9 ± 11.1	−86 ± 36
Cl^-	40	38.4 ± 2.9	6.57 ± 0.81				
	50	101 ± 1	20.5 ± 0.5				
	60	257 ± 15	34.1 ± 3.9	80 ± 1	−36 ± 2	64.5 ± 23.3	−98 ± 72
CF_3COO^-	40	10.2 ± 0.4					
	50	38.6 ± 0.9					
	60	121 ± 4		104 ± 3	29 ± 10		
H_3PO_4	40	3.03 ± 0.20	7.58 ± 0.87				
	50	15.2 ± 1.9	22.6 ± 4.2				
	60	44.6 ± 2.4	69.8 ± 12.8	113 ± 7	49 ± 20	93.2 ± 2.3	−7.4 ± 7
$H_2PO_4^-$	40	10.3 ± 0.5	0.18 ± 0.06				
	50	28.9 ± 4.6	0.65 ± 0.20				
	60	87.5 ± 10.2	3.60 ± 0.87	89.2 ± 2	−17 ± 6	130 ± 12	77 ± 37

[a] Derived from the second order rate constants.

TABLE 4. Comparison of the kinetic parameters for the reactions studied with those for the analogous systems with R = H and Me (T = 60 °C, I = 1.0 ($LiClO_4$))

Anating species	10^4k_+K (M^{-1} s^{-1})			$\Delta G^‡_+$ (kJ mol^{-1})		
	R = H	R = Mc	R = Et	R = H	R = Me	R = Et
Br^-	4.40 ± 0.37[a]	179 ± 5[a]	222 ± 1[b]	104[a]	93[a]	92
Cl^-	2.90 ± 0.54[a]	212 ± 9[a]	257 ± 15	104[a]	93[a]	92
CF_3COO^-	1.36 ± 0.03[a]	80.6 ± 3.3[a]	121 ± 4	107[a]	95[a]	94
H_3PO_4		23.8 ± 2[a]	44.6 ± 2.4		98[a]	97
$H_2PO_4^-$	1.54 ± 0.2[c]	52.7 ± 3.1[a]	87.5 ± 10.2	106[c]	96[a]	95

[a] Ref. 5. [b] Extrapolated from Eyring plots. [c] Ref. 10.

Nevertheless, the increase in these rate constant values is smaller than that observed on going from R = H to R = Me. This is not surprising when one takes into account the estimated cone angles for the RNH_2 (R = H, Me, Et) amine series. Although an important difference on the steric hindrance is expected on going from R = H to Me (94 to 106°), the cone angle values estimated for the R = Me and Et substituted amines are the same [11]. This is also observed in the electronic spectra values: although Δ_0 goes from 21 270 to 20 500 cm^{-1} on changing from R = H to Me [5, 12], the difference on going further in the alkyl chain in the amine is very small, $\Delta_0 = 20\,250$ cm^{-1} for R = Et, indicating that changes in the complex structure in solution are minimal. The same can be observed for the activation parameters for the anation reactions studied; even though there is a definite decrease in the activation free energy at 60 °C for the reactions on going from NH_3 to $MeNH_2$ of about 10 kJ mol^{-1} [5], no decrease in $\Delta G^{\ddagger}{}_{+}$ is observed on going from $MeNH_2$ to $EtNH_2$, indicating that isokinetic plots for R = Me and Et are the same and different from that for R = H (Fig. 1).

The comparison of the crystal structure (Fig. 2) of the $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$ compound with that of $[Co(NH_3)_5H_2O](IO_3)_3 \cdot H_2O$ [13] and $[Co(NH_3)_5H_2O](S_2O_6)_3 \cdot 2H_2O$ [14] is in very good agreement with the observed kinetic trends. Taking into account the I_d nature of the reactions studied, any increase on the steric demands of the inert ligands in the ground state could be, although not necessarily [15], related to an acceleration on the substitution reactions. Table 5 shows selected bond distances and angles for the title complex as well as those for two known structures with R = H. The errors involved in the $[Co(EtNH_2)_5H_2O](ClO_4)_3 \cdot 2H_2O$ structure are slightly larger than those for the $[Co(NH_3)_5H_2O]^{3+}$ analogues, nevertheless an overall trend can be seen. Although the Co–O distance appears to be slightly shorter for the bulkier amine complex, the effect is fully offset by the larger average O–Co–N_{cis} angles when compared with those for the pentaammine cation. On the other hand, even though the Co–N_{trans} distance is only slightly larger for the $EtNH_2$ complex, all the Co–N_{cis} distances are longer for the larger amines in order to compensate both for the steric demands of the ethyl group and the larger O–Co–N_{cis} angles found. This indicates that, as already pointed out very recently [16], the greater steric demands of the amine ligands are mostly offset by a lengthening of the Co–N_{cis} distances.

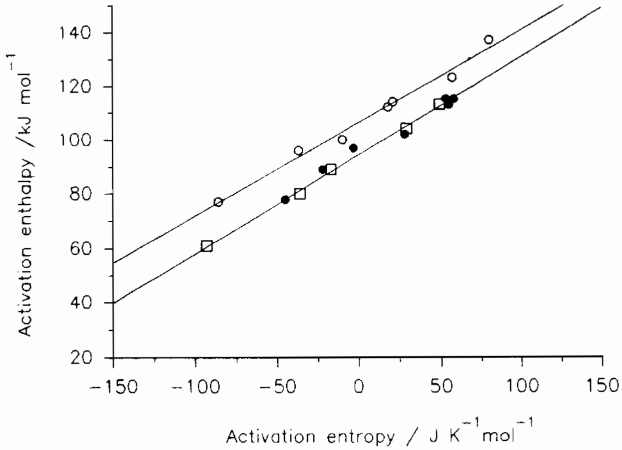


Fig. 1. Isokinetic plots for the $[Co(RNH_2)H_2O]^{3+}$ anation reactions studied. R = H (○), CH_3 (●), CH_3CH_2 (□).

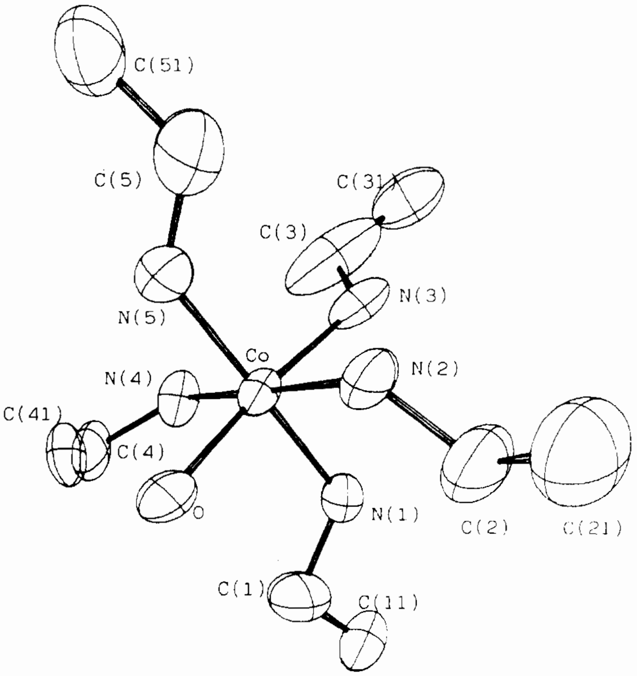


Fig. 2. ORTEP projection of the $[Co(EtNH_2)_5H_2O]^{3+}$ ion indicating atom numbering.

TABLE 5. Selected angles and bond distances for the $[Co(RNH_2)_5H_2O]^{3+}$ (R = H, Et) complex cations

Complex ion	d(Co–O) (Å)	d(Co–N_{trans}) (Å)	d(Co–N_{cis}) (Å)	N_{cis}–Co–O (°)
R = H	1.954(1)^a	1.952(1)^a	1.972(1)^a 1.950(1)^a 1.975(1)^a 1.958(1)^a 1.964^{a,c}	89.5^{b,c}
	1.968(7)^b	1.965(8)^b	1.961(9)^b 1.956(7)^b 1.974(8)^b 1.957(8)^b 1.962^{b,c}	89.5^{a,c}
R = Et	1.939(7)	1.992(10)	2.021(11) 1.981(10) 2.041(12) 1.971(12) 2.003^c	90.1^c

^{a}Ref. 14, dithionate salt. ^{b}Ref. 13, iodate salt. ^{c}Average value.

Conclusions

Taking into account that a Co–OH_2 π-bonding in these complexes is very unlikely, all the differences observed in the reaction rate constants and thermal activation parameters ought to be due to the steric hindrance of the systems studied. Nevertheless, solvation effects could also account for the differences observed, the specific solvation of pentaammine complexes should be different from that of pentakis(alkylamine). In this respect, comparison of the crystal structures of $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(EtNH_2)_5H_2O]^{3+}$ cations shows a significative effect on the increase of the size of the amine ligand, thus providing a straight forward explanation for the increase on reaction rate constants observed for the anation reactions of the $[Co(RNH_2)_5H_2O]^{3+}$ systems on going from R = H to R = Me or Et. The greater steric requirements of the amine ligands, when compared with those from the ammine, favour the dissociation of the leaving group and so enhance the reaction rate of an I_d substitution reaction; evidently the difference in rate constants should be much larger between NH_3 and $MeNH_2$ than between $MeNH_2$ and $EtNH_2$ given the fact that the steric requirements practically do not change in the latter. Again, this is made very clear in the isokinetic plots for the reactions studied showing that, while a gap between the R = H and R = Me plots is present, the R = Et plot coincides with that for R = Me.

Supplementary material

Tables of observed rate constants (2 pages), bond lengths and angles (1 page), final atomic coordinates (2 pages), anisotropic thermal parameters (1 page), observed and calculated structure factors (7 pages) are available from the authors on request.

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